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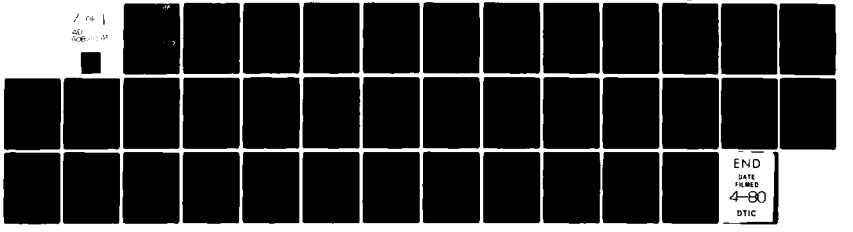

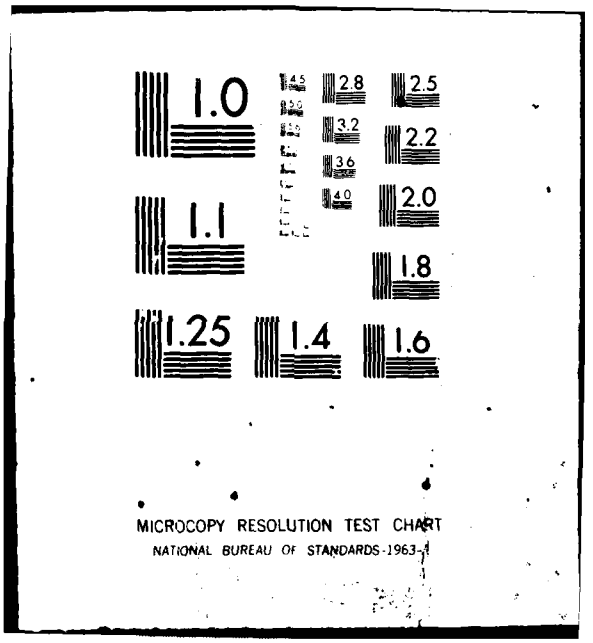
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(2) LEVEL II

ISS-SIMS AND AES-SIMS CHARACTERIZATION OF MICA SURFACES

W. L. BAUN

MECHANICS & SURFACE INTERACTIONS BRANCH
NONMETALLIC MATERIALS DIVISION

J. S. SOLOMON

UNIVERSITY OF DAYTON RESEARCH INSTITUTE
300 COLLEGE PARK
DAYTON, OHIO 45469

JANUARY 1980

TECHNICAL REPORT AFML-TR-79-4203
Final Report for period July 1977 — July 1979

AIR FORCE MATERIALS LABORATORY
AIR FORCE WRIGHT AERONAUTICAL LABORATORIES
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This technical report has been reviewed and is approved for publication.

W. L. BAUN, Project Engineer
Mechanics & Surface Interactions Br.
Nonmetallic Materials Division

S. W. TSAI, Chief
Mechanics & Surface Interactions Br.
Nonmetallic Materials Division

FOR THE COMMANDER

J. M. KELBLE, Chief
Nonmetallic Materials Division

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Secondary Ion Mass Spectrometry (SIMS), Ion Scattering Spectrometry (ISS), and Auger Electron Spectrometry (AES) are used to characterize mica surfaces. The results on matching cleaved surfaces show that cleavage occurs along the potassium layer and the potassium ions are shared equally between the separated surfaces. A comparison of these freshly cleaved surfaces with original weathered surfaces show large differences in the potassium (OVER)

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20. ABSTRACT (Continued)

content. Perhaps very slow potassium depletion takes place from mica surfaces under ambient conditions. Other ISS/SIMS data from treated mica surfaces show a high sensitivity for small chemical changes which take place on these surfaces. The experiments indicate that ISS/SIMS technique should prove very useful for diffusion studies through thin films using mica surfaces.

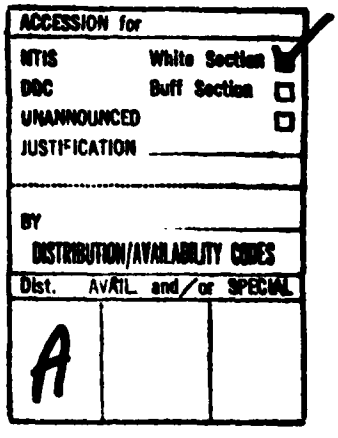
9. PERFORMING ORGANIZATION NAME AND ADDRESS (Continued)

University of Dayton Research Institute
300 College Park
Dayton, Ohio 45469

FOREWORD

This technical report was prepared by W. L. Baun of the Mechanics and Surface Interactions Branch, Nonmetallic Materials Division, Air Force Materials Laboratory. The work was initiated under Project 2419, "Nonmetallic and Composite Materials" and WUD No. 44, "Improved Materials, Processes, and Life Prediction Methodology of Adhesive Bonding" monitored by T. W. Haas.

This report covers work conducted inhouse during the period July 1977 - July 1979.



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INTRODUCTION

In the past, the surface of mica has been characterized by Low Energy Electron Diffraction (LEED) and Auger Electron Spectrometry (AES)[1,2,3] and more recently by a static SIMS (SSIMS)[4] method. These papers have dealt with surface characterization after cleaning and cleaving procedures. The recent paper on static SIMS characterization took advantage of the great sensitivity of SIMS and used the detailed information about molecular cluster species present on the surface, and their relation to the sources of surface contamination. The purpose of the present investigation is surface characterization of mica family substrates for vacuum deposition of thin films. These thin films will then be used to study diffusion under various conditions as a part of a larger study to compare the diffusion found in polycrystalline materials primarily by grain boundary diffusion with that found in diffusion through single crystal materials, such as alkali halides. This diffusion, particularly of alkali elements sodium and potassium has important technological implications in numerous fields, such as adhesive bonding, microencapsulation, and thin film technology.

EXPERIMENTAL

The characterization methods used in this work are the combined ISS/SIMS and AES/SIMS as seen in Figures 1 and 2. The same primary ion beam is used to probe the surface in both ISS and SIMS. The scattered ion energy spectrum is produced by the electrostatic spectrometer (90^{o} scattering) and is representative of the elements occupying the first atomic layer at the surface.[5] The primary ion beam, which in this case has an energy 100-2500 eV, also sputters away surface atoms which are ionized and detected by the quadrupole mass analyzer.[6] The system used here is the commercial ion scattering spectrometer Model 520 manufactured by 3M Co., St. Paul, MN) to which a modified (UTI (Uthe Technology International, Sunnyvale, CA) Model 100C quadrupole mass filter has been added to allow positive SIMS. A simple three-element cylindrical energy analyzer was added to the mass filter. The ISS instrument was updated during this work with a cylindrical mirror analyzer (CMA) to give higher intensities and scattering at 138^{o}. The spectra obtained with the CMA are marked on the figures. The experimental arrangement using the CMA is seen in Figure 3.

AES data was obtained with a Model 540 Thin Film Analyzer (Physical Electronics, Inc., Eden Prairie, MN) equipped with a simple SIMS system similar to that used with ISS.

Since mica is such a good insulator, it acquires a charge upon bombardment with either electrons or with positive ions. Electron or positive ion bombardment causes the ejection of secondary electrons from the surface, causing a build-up of a positive charge on the surface. Czanderna and co-workers[7] have shown this charge build-up can exceed hundreds of volts in certain cases. The effect of this charge build-up on ion scattering spectra is to shift the ion scattering peaks from the energy ratio at which they should occur. Large charge build-up may result in virtually complete reflection of the primary ions and

the spectrum disappears. Likewise the acquisition of positive charge on the specimen causes the SIMS and AES data to rapidly deteriorate. In order to compensate for this positive build-up, low energy electrons are sprayed on the surface to equalize the charge as shown by Muller.[8] The low energy electrons are increased until the ion scattering peaks are returned to the correct point which corresponds to a voltage on the sample of zero volts.

Except where noted, all experiments shown here are using high-purity ASTM V-3 African ruby mica (muscovite) obtained from Asheville Schoonmaker Mica Co., Newport News, VA.

RESULTS AND DISCUSSION

Mica was chosen as substrate material for this work because of its ready availability in single crystal form and its thermal stability (up to about 700°C).[1] It can be reproducibly cleaved under various atmospheres to produce extremely smooth surfaces. Mica is a sheet silicate and the sheets are linked by single layers of potassium ions as shown in Figure 4. Cleavage takes place along the potassium layer as shown, and half of the potassium ions are shared by each face in a random distribution. The equal distribution of potassium on each face of a cleaved specimen is shown in Figures 5 and 6. In this experiment, a very thin sheet was cleaved in air from a thicker block of mica. The thin cleaved section was subjected to ISS and SIMS analysis and gave the data shown in Figure 5. Experimental conditions were kept constant for the data shown in Figure 6. Virtually identical data is obtained from the two cleaved specimens. The original as received surface, however, is much different, showing in Figure 7 approximately half as much potassium on the surface compared to a freshly cleaved surface. Poppa and Elliott[1] have shown the depletion of potassium upon heating. Perhaps there is a very slow depletion which takes place under ambient conditions, even when the surface is not heated above room temperature. In addition to the difference of potassium shown in the ion scattering spectra there are some differences observed in the positive SIMS data also. Because of the uncertain and rapidly changing ion yields with oxidation and other factors, the absolute peak heights may not be meaningful in positive SIMS. However, as can be seen, there are changes in the ratios of the major peaks and in addition, there is a definite change in the molecular peaks in the region of mass 43-45 where AlO^+ and other unidentified molecular peaks exist.

Freshly cleaved surfaces were boiled in deionized H_2O for 30 minutes. ISS and SIMS spectra are shown from this surface in Figure 8. No apparent change is seen in the ion scattering spectrum, but considerable differences are seen in the positive SIMS data. The appearance of appreciable amounts of magnesium may have come from magnesium leached from the mica and substituted

octahedrally back onto the surface for the aluminum or this may represent a minute quantity of magnesium that was originally present in the deionized water. Also, there is an increase in the molecular species AlO^+ in comparison with the $^{41}K^+$ peak as shown in the positive SIMS spectrum.

A freshly cleaved surface was also held for 30 minutes in one molar sodium hydroxide solution. The ion scattering positive SIMS data are shown in Figure 9. Again there is little obvious change in the ion scattering spectrum. The positive SIMS spectrum, however, shows that apparently a large amount of sodium has substituted on the surface with the potassium originally present. Immersion in the sodium hydroxide solution does not appear to change the abundance of the AlO^+ molecular species.

Figure 10 shows the ISS/SIMS data for a freshly cleaved surface of an impure mottled inhomogeneous mica of unknown origin. The ion scattering spectrum is less distinct, but is the general shape as that shown for the earlier freshly cleaved surfaces from pure African mica. Likewise, the positive SIMS surface are very similar and surprisingly very few extra peaks are observed. In another spectrum in a different spot in a darkened area, appreciable amounts of iron were observed.

Ion Scattering Spectra of muscovite and two other mica family members, biotite and phlogopite are shown in Figures 11-13. These spectra were obtained using the CMA and the apparatus shown in Figure 3. The spectrum for muscovite is similar, of course, to the spectra obtained at 90^o but there is better dispersion and the background is lower. Spectra of biotite (Figure 12) and phlogopite are also similar, but show the substitution of other ions in the sheet silicate structure, namely fluorine. The ratios of certain elements such as magnesium to iron determine the exact nomenclature for the mineral[9]. The occurrence of impurity and substitutional ions is especially obvious in SIMS spectra. A summary of ions observed in + SIMS for muscovite, biotite and phlogopite is seen in Table I along with a listing of ion species observed in - SIMS.

AES Data are shown in Figures 14 through 21 for African mica, Canadian muscovite, biotite and phlogopite. Especially interesting is the difference in spectra between original surfaces and "equilibrium sputtered" surfaces. "Equilibrium sputtering" represents sputtering until AES data stabilize and no further changes are seen with increasing sputtering. It is recognized that this is a damaged surface which does not necessarily represent true composition, but it is a surface which may be easily reproduced from laboratory to laboratory or from day to day in the same laboratory.

Elemental sputter profiles, such as those in Figure 19, can provide depth distribution information of sputtering rate calibrations are made. In the case of phlogopite, the profiles did not reflect the expected repetitive K rich layers. This was probably due to a combination of electron and ion beam effects which result in decreased depth resolution.[10-11]

SUMMARY AND CONCLUSIONS

These results indicate the powerful potential of the combination of modern methods of surface analysis to characterize freshly cleaved surfaces of mica. The excellent sensitivity and adjacent atom resolution of positive SIMS and AES and the first surface sensitivity of ion scattering make these techniques ideal for studying such surfaces. These same characteristics will make these techniques very valuable for studying diffusion from a mica surface through thin films. The insulating qualities of mica make it more difficult to obtain spectrochemical data but these difficulties may be overcome. It remains to be seen whether the heating of the electron beam in AES negate the technique for diffusion studies on highly mobile ions.

TABLE I

COMPARISON OF POSITIVE AND NEGATIVE
SIMS DATA FOR MICA FAMILY MINERALS

+ SIMS	Strong	Medium	Weak
Muscovite	K^+	Na^+, Al^+	CHn^+, Si^+, AlO^+
Biotite	K^+	F^+, Na^+ Mg^+, Al^+	CHn^+, Si^+, Fe^+
Phlogopite	K^+	Na^+ Al^+ F^+	CHn^+, Mg^+, Si^+
- SIMS			
Muscovite	O^- (very strong)	none	amu 24, 26, 28, 32 amu 35, 37 (Cl^-) 43 (AlO^-) 59 (AlO_2^-) 60 (SiO_2^-)

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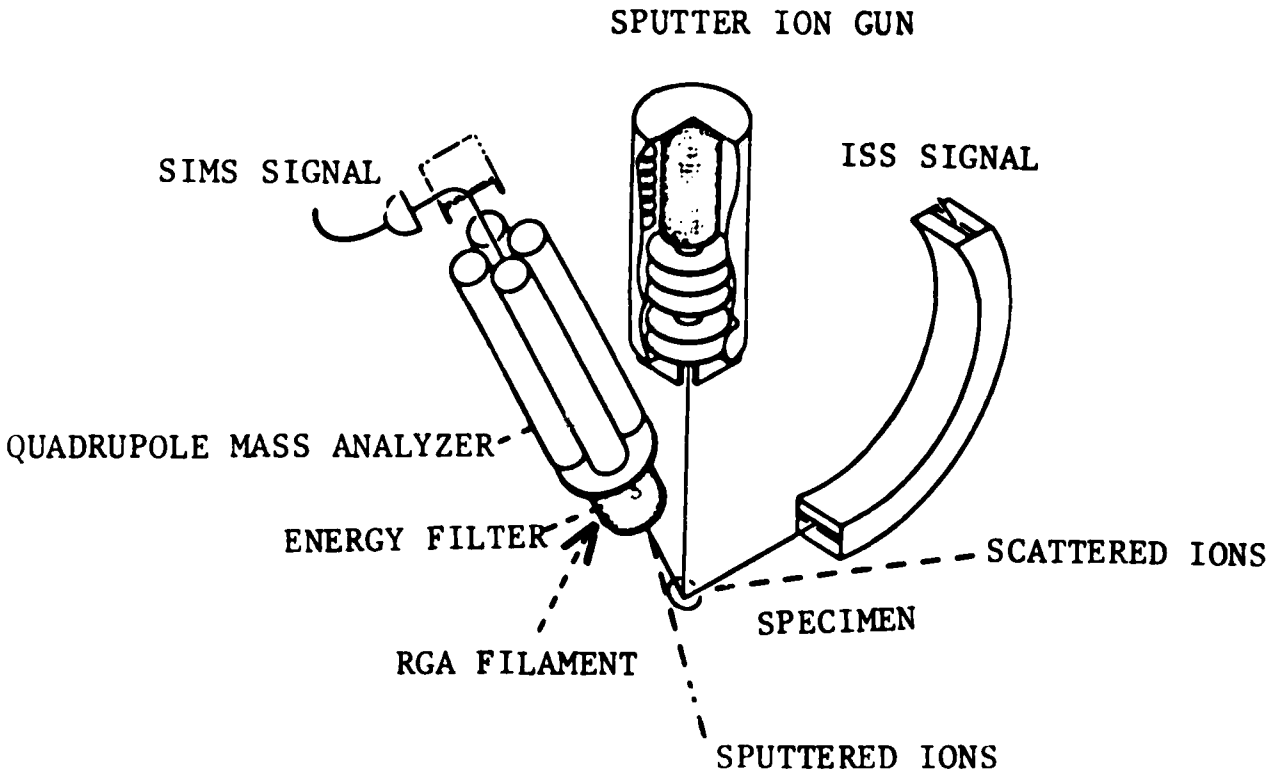

Figure 1. Components in UHV for Ion Scattering (90^{o}) and Secondary Ion Mass Spectrometries

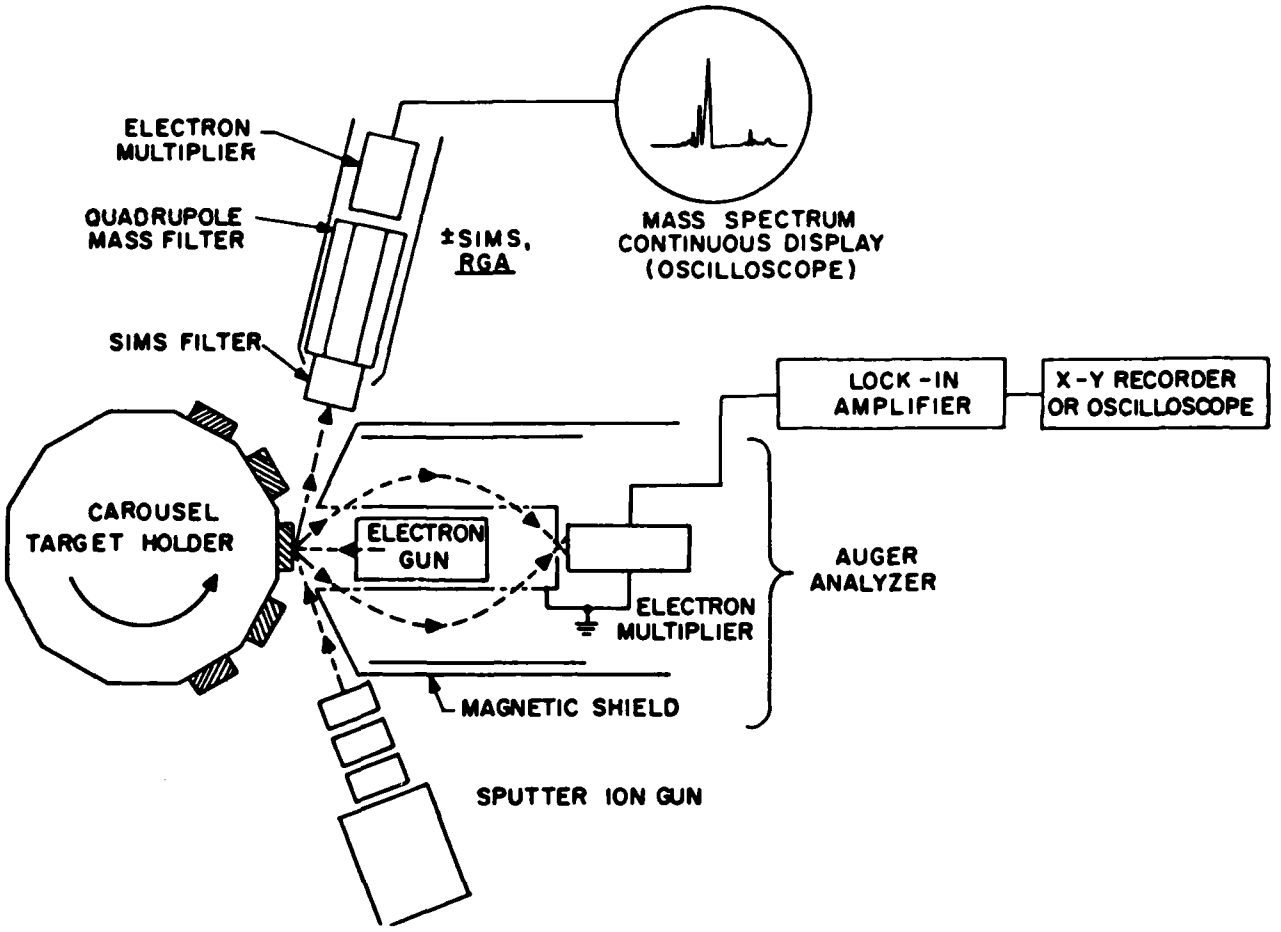

Figure 2. Components in UHV for AES/SIMS

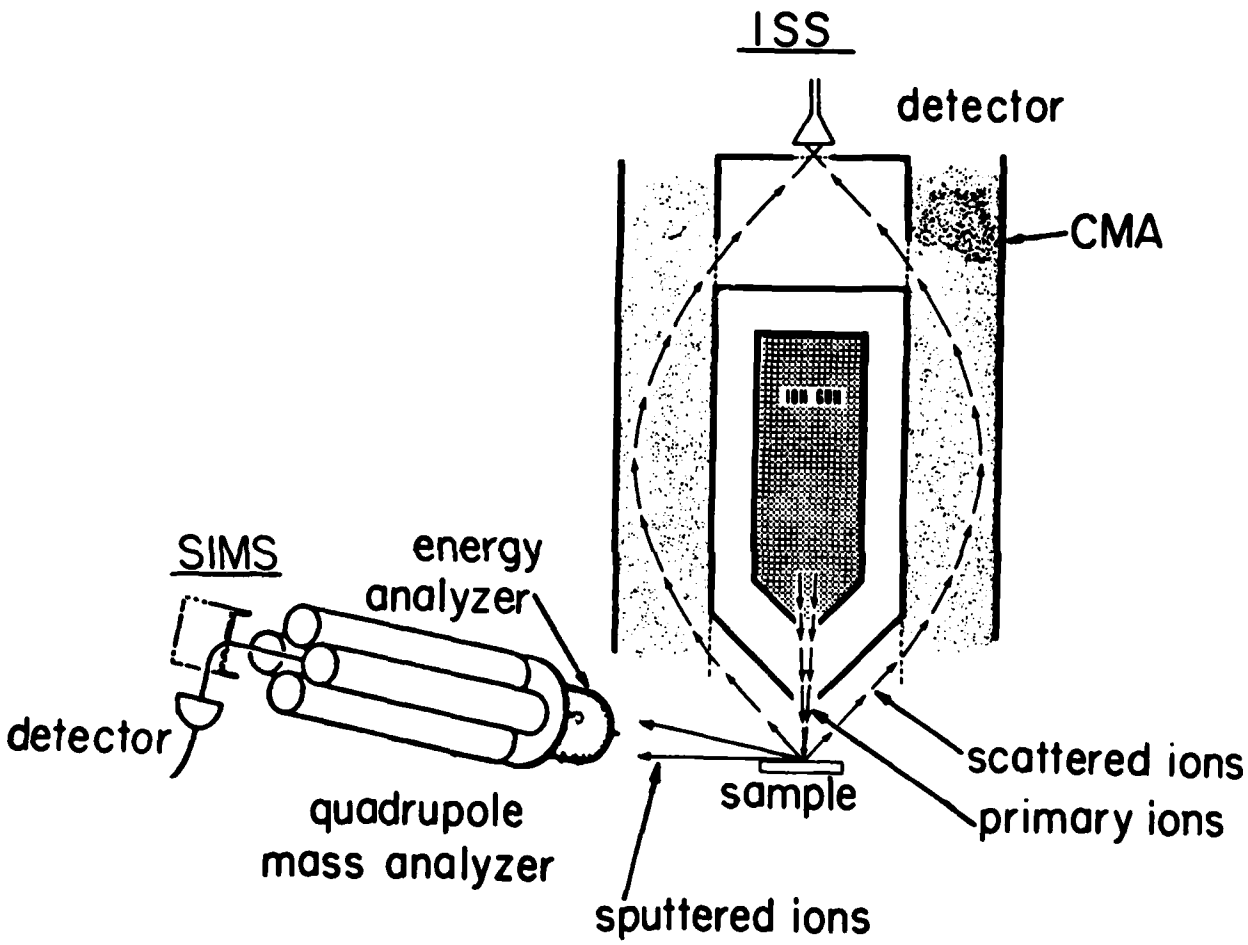

Figure 3. Components in UHV for ISS (138°) with CMA and SIMS

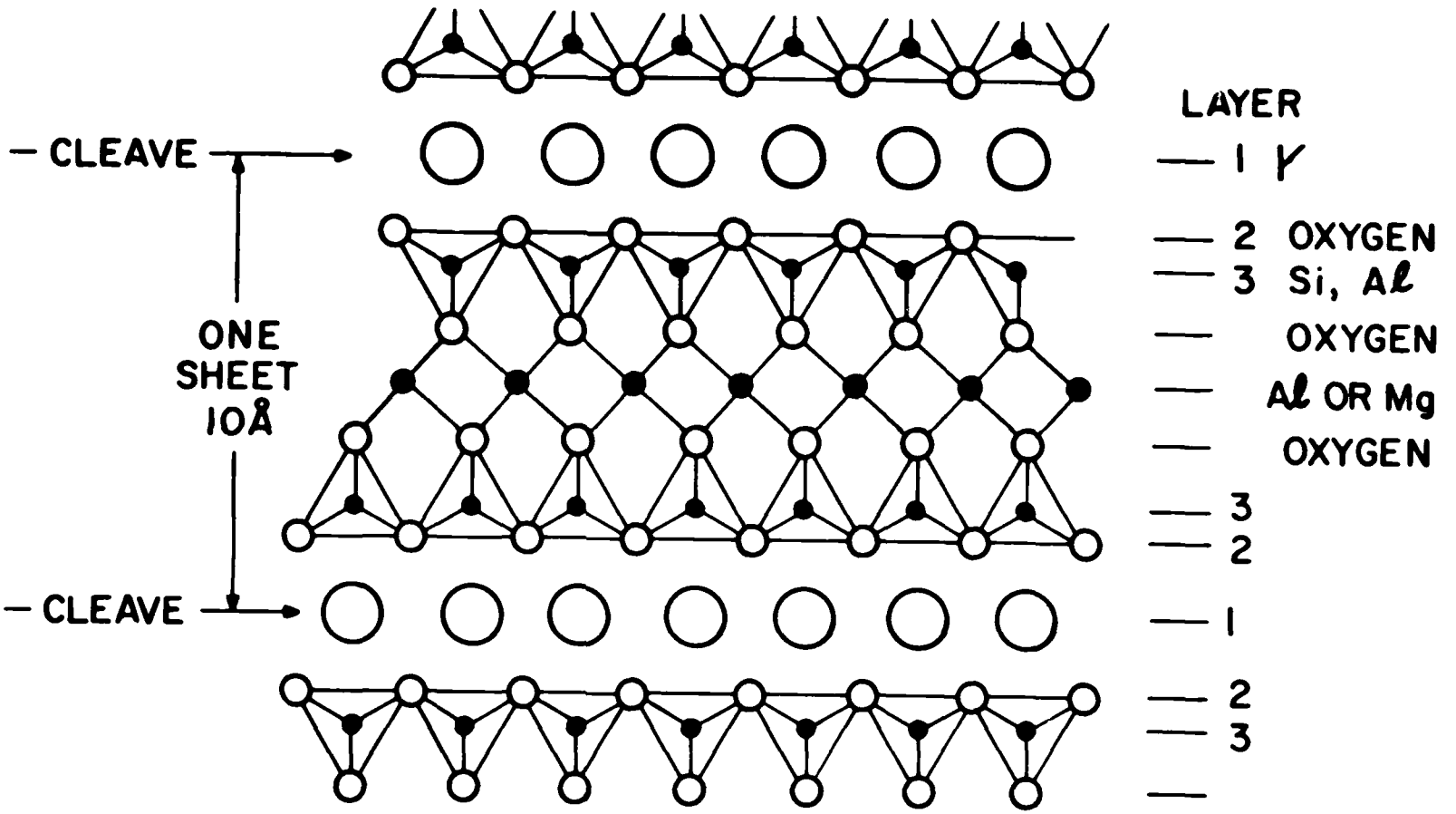

Figure 4. Structural Representation of Mica (Muscovite as used here contains aluminum in the center layer).

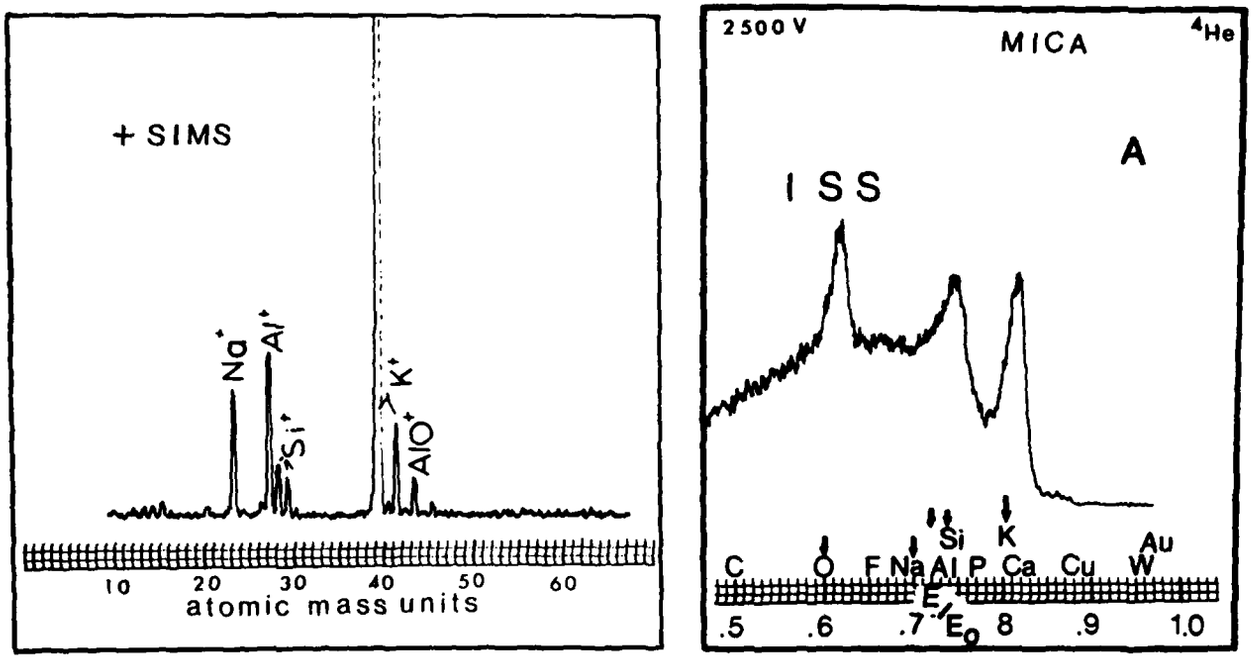

Figure 5. ISS-SIMS Data from a Thin Cleaved Section of Mica.

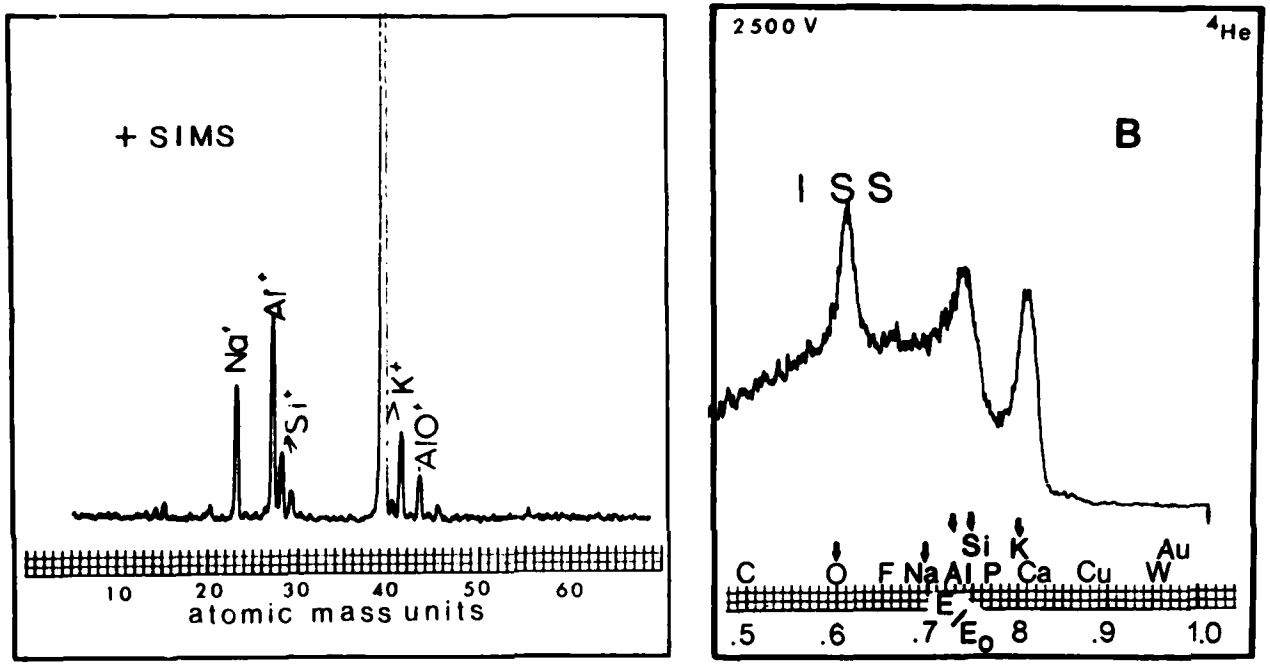

Figure 6. ISS-SIMS Data from a Thick Cleaved Section of Mica (The matching cleaved surface from the thin sample in Figure 2).

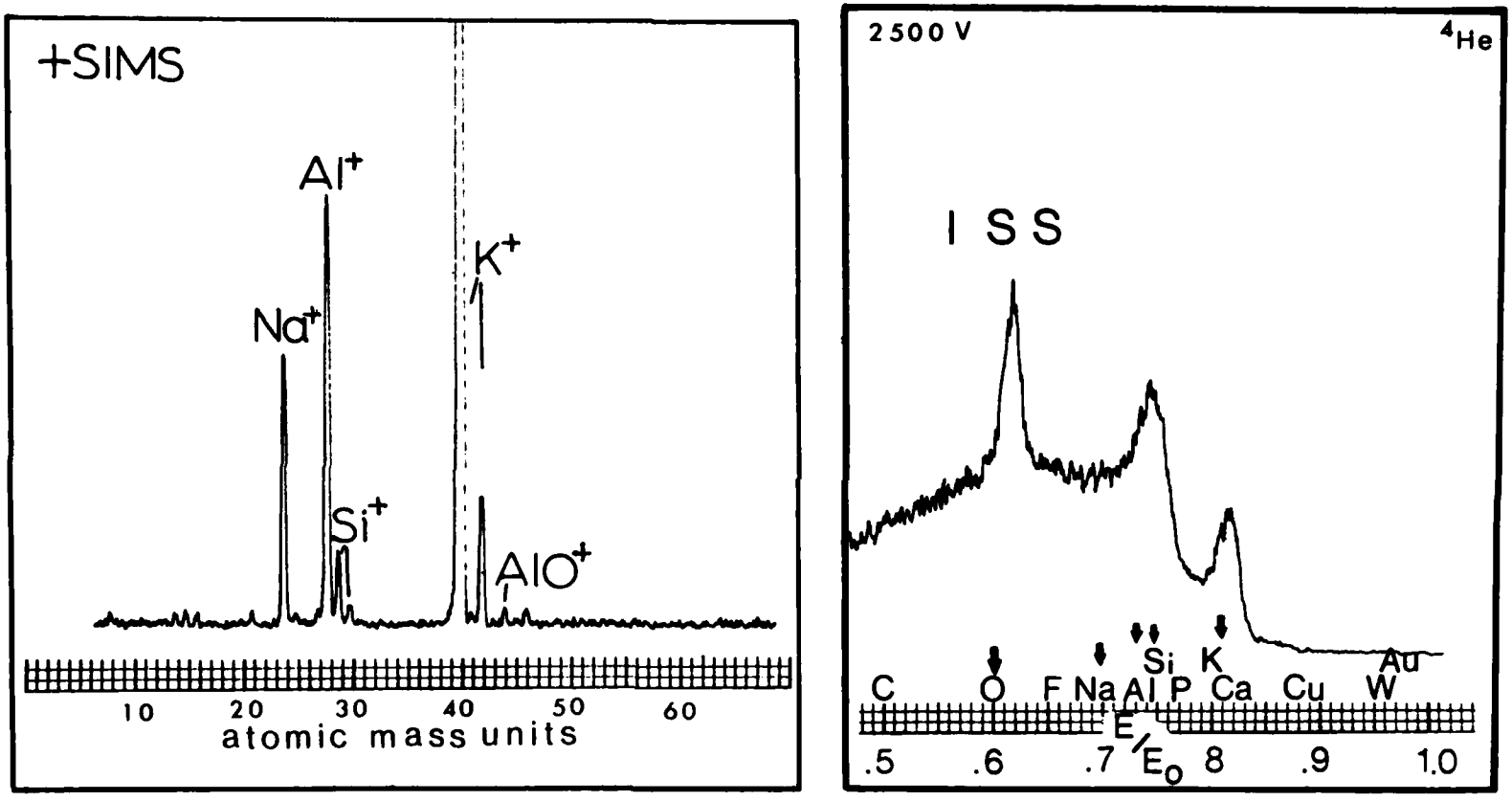

Figure 7. ISS-SIMS Data from Aged Surface of Mica.

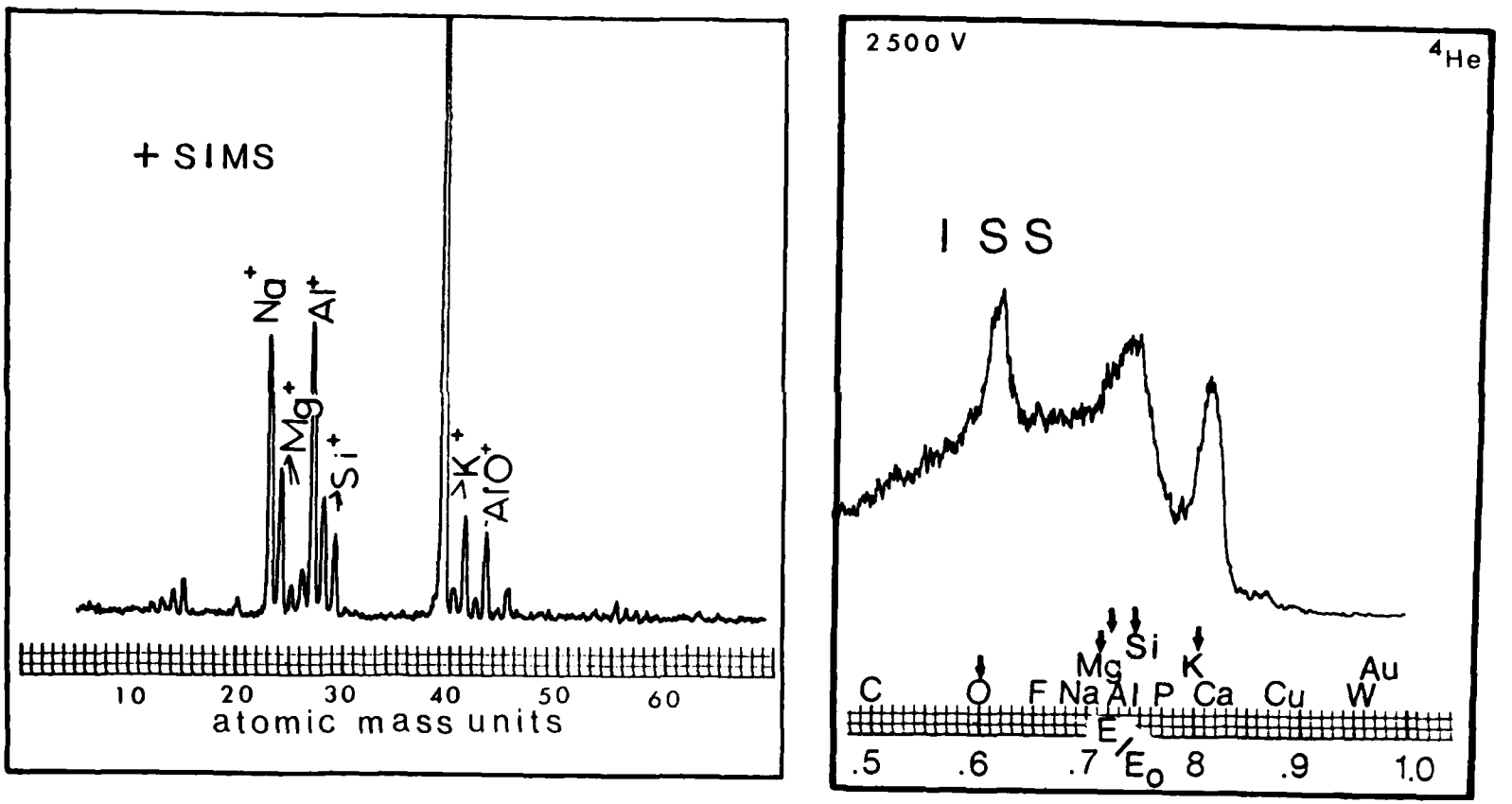

Figure 8. ISS-SIMS Data from Freshly Cleaved Surfaces Boiled for 30 minutes in dI H_2O.

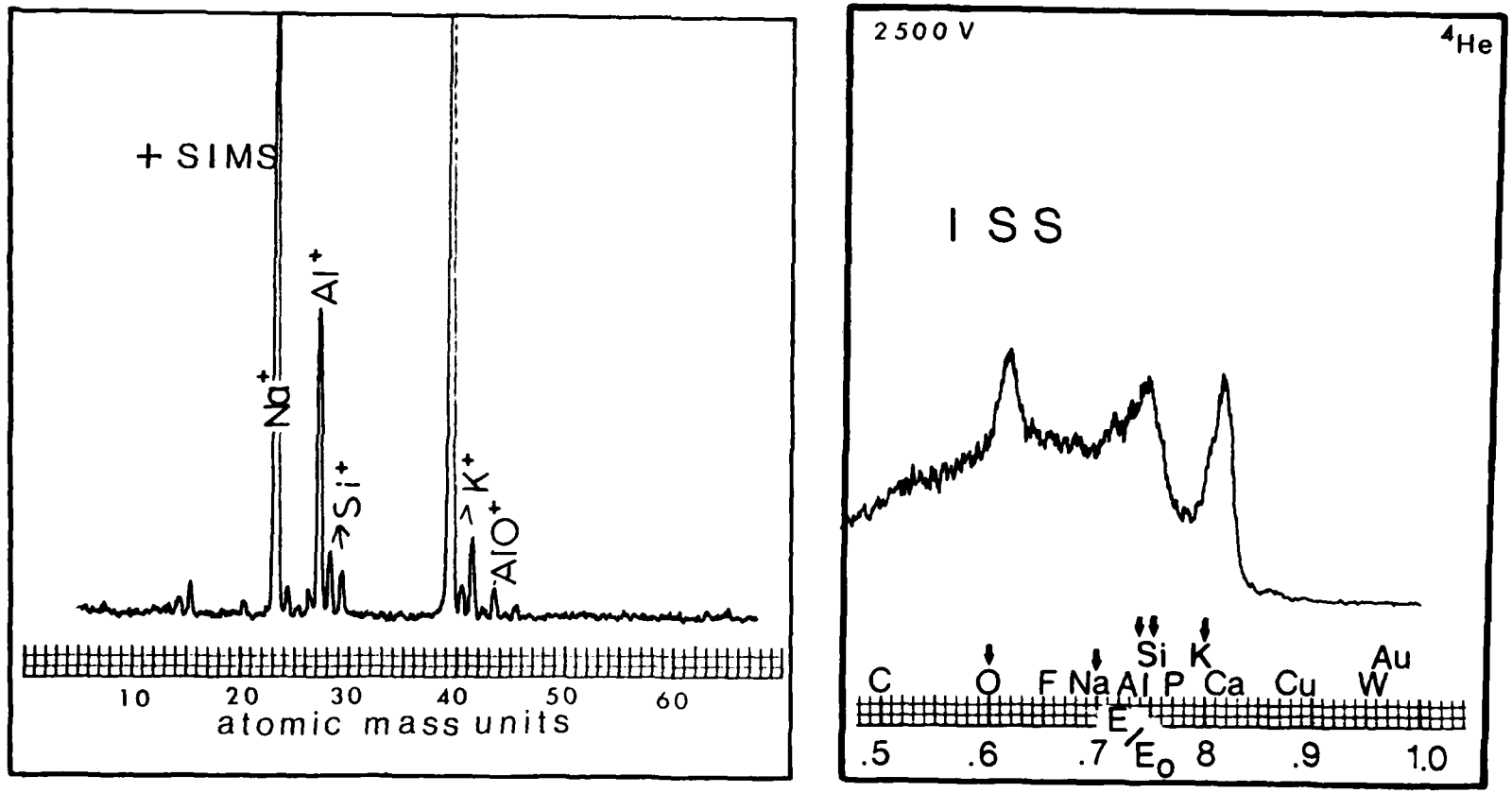

Figure 9. ISS-SIMS Data from Freshly Cleaved Surface Soaked in NaOH (IM) for 30 Minutes.

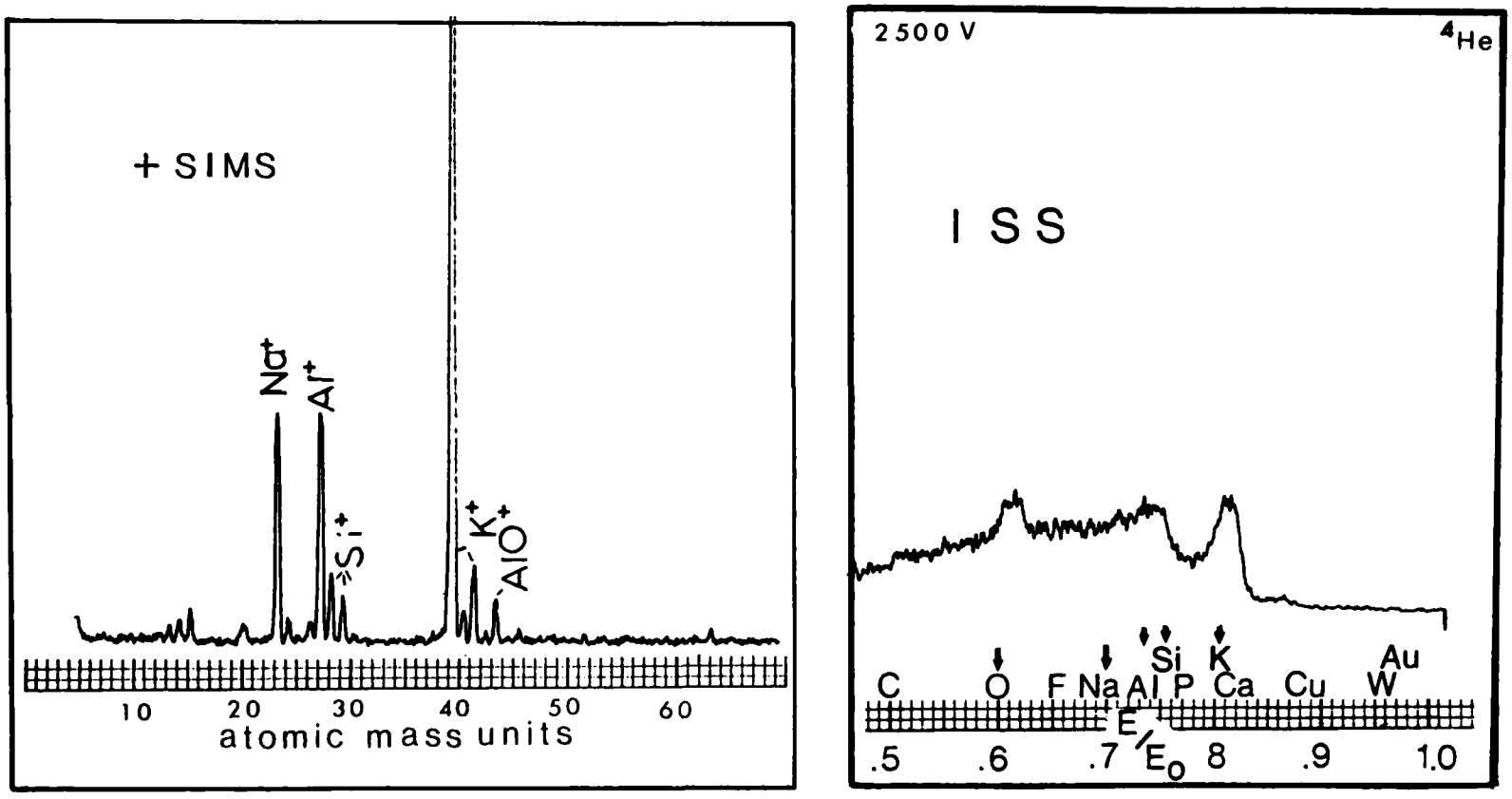

Figure 10. ISS-SIMS Data from a Freshly Cleaved Surface of a Mottled Mica of Unknown Origin.

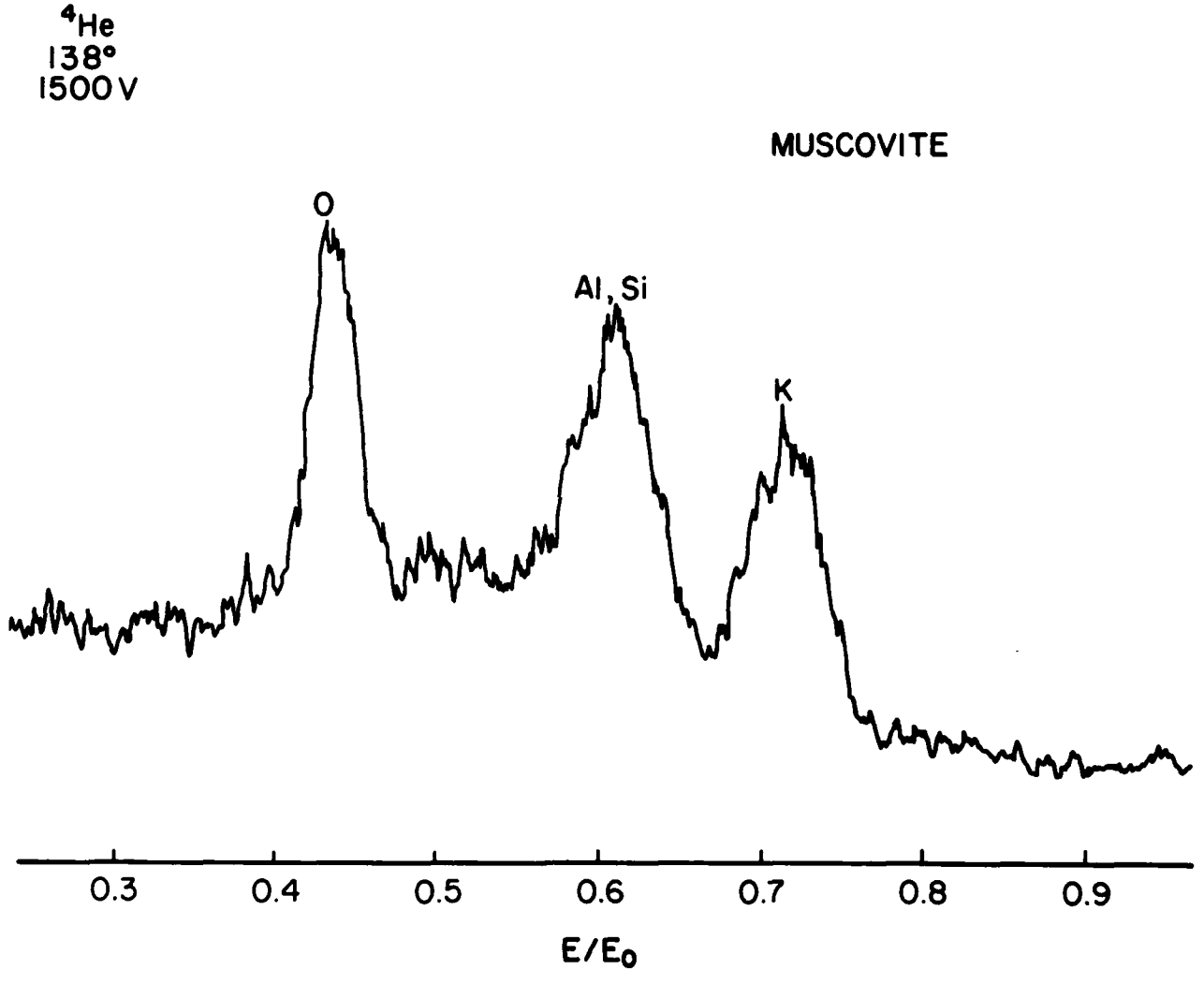

Figure 11. ISS Data Using the CMA for Muscovite.

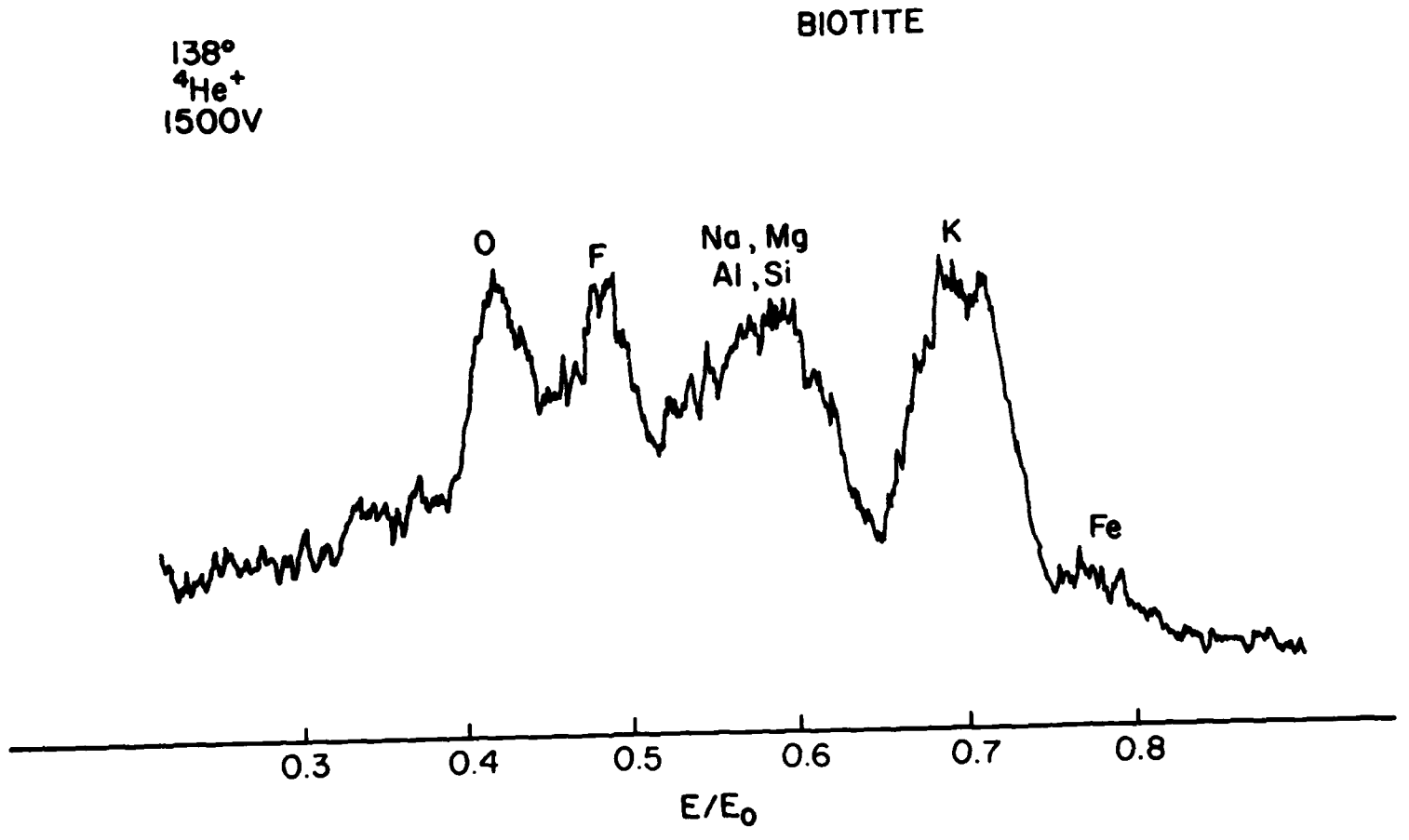

Figure 12. ISS Data Using the CMA for Biotite.

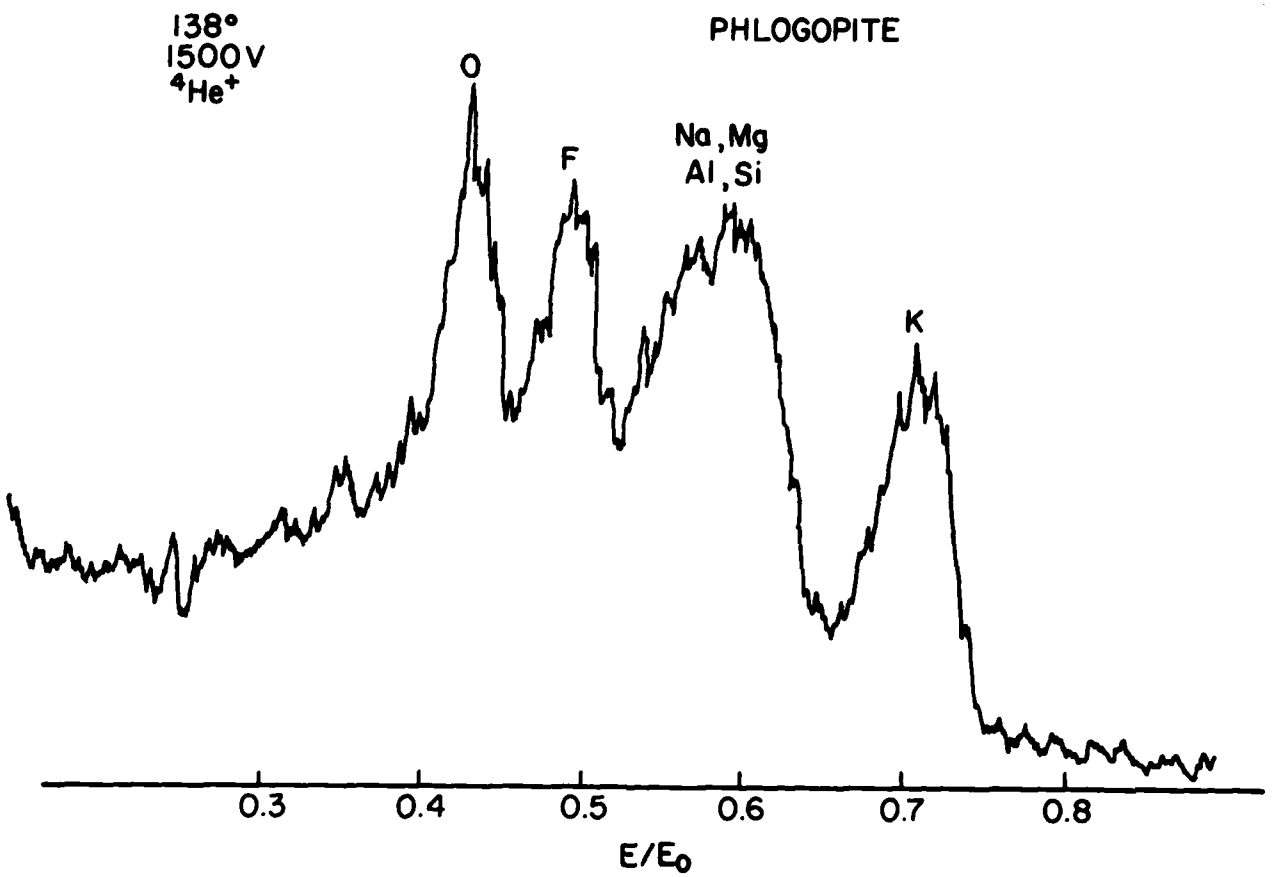

Figure 13. ISS Data Using the CMA for Phlogopite.

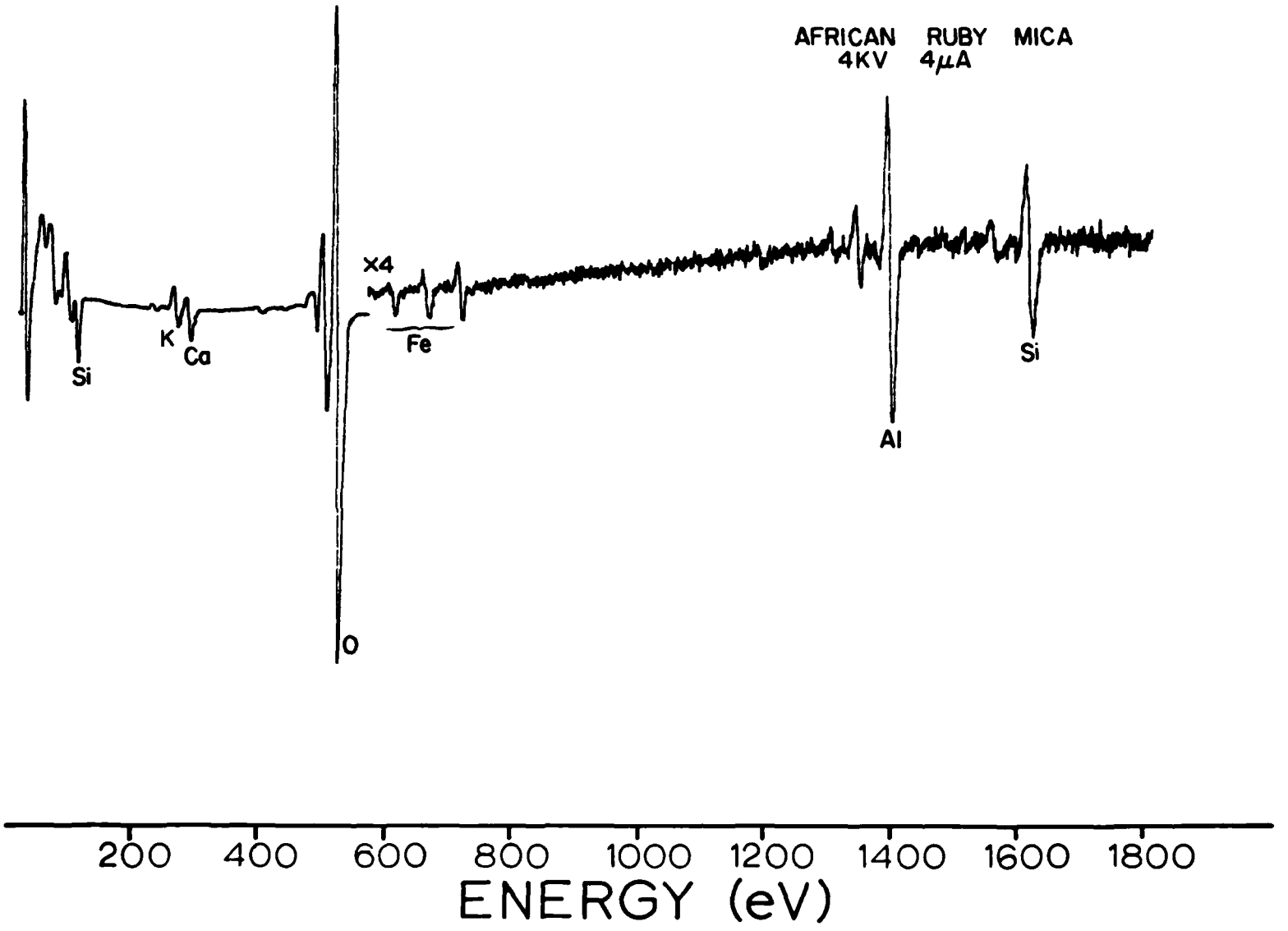

Figure 14. AES Data for African Ruby Mica.

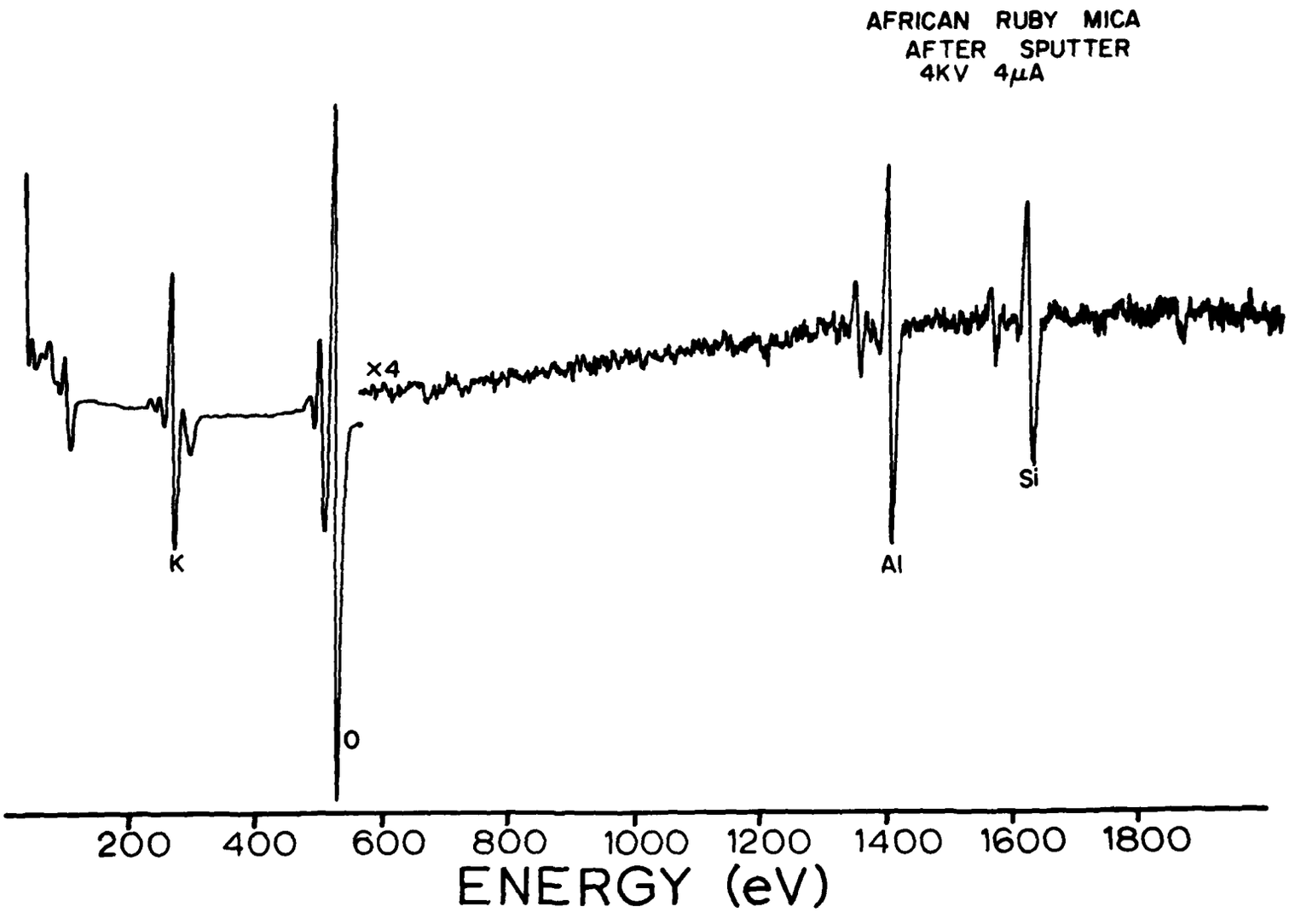

Figure 15. AES Data for African Ruby Mica after "Equilibrium Sputter".

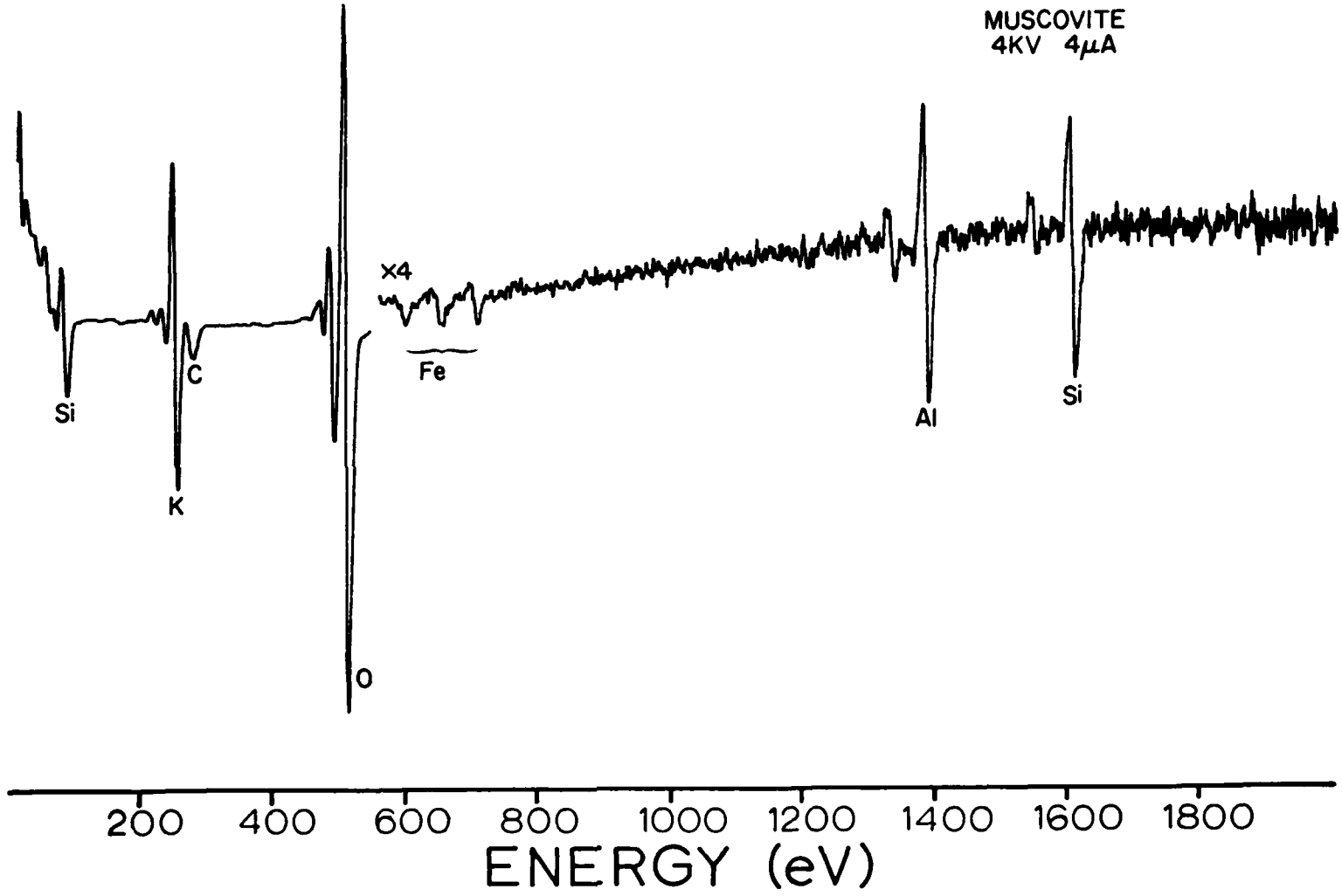

Figure 16. AES Data for Muscovite.

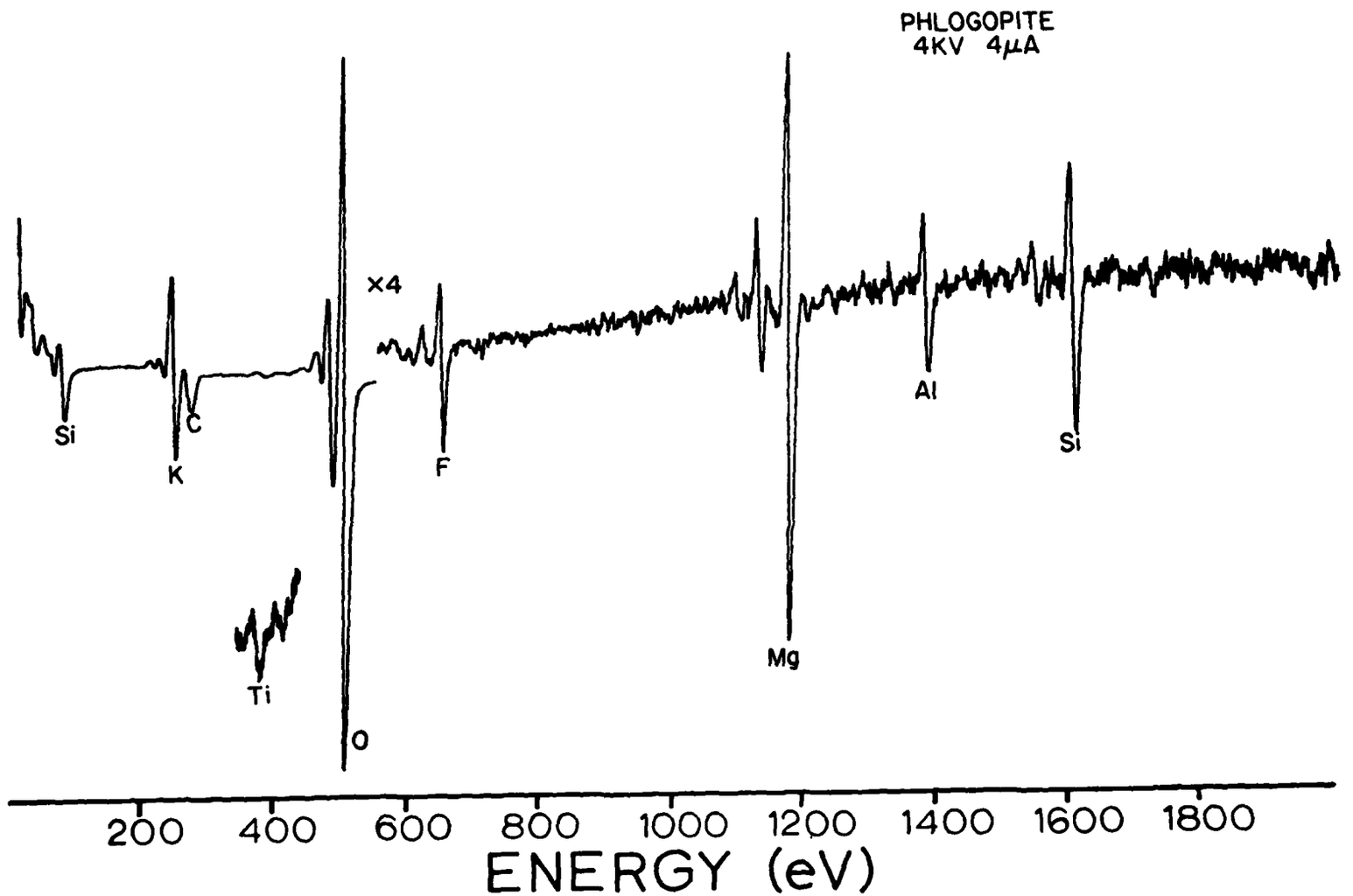

Figure 17. AES Data for Phlogopite.

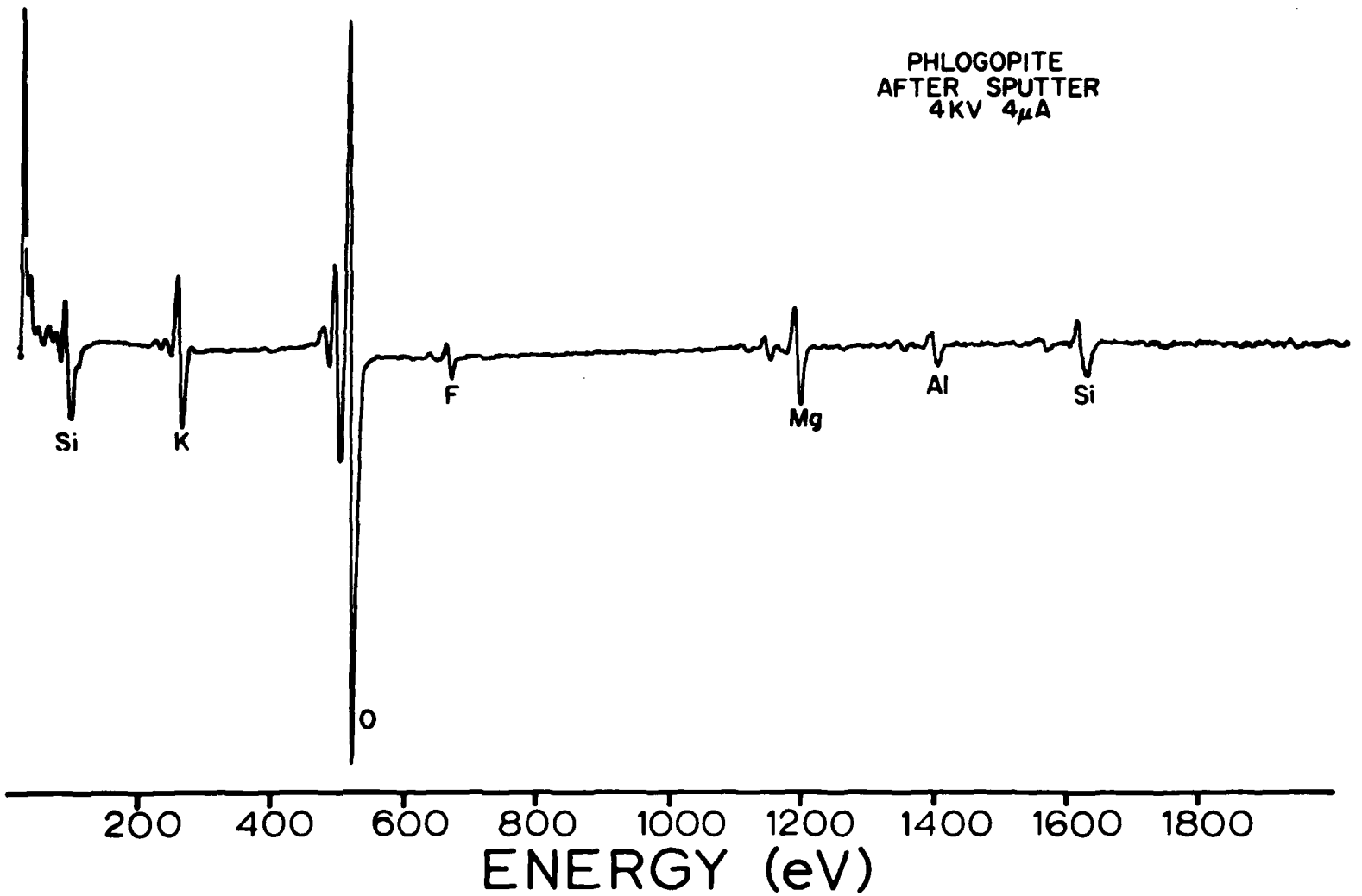

Figure 18. AES Data for Phlogopite after "Equilibrium Sputter".

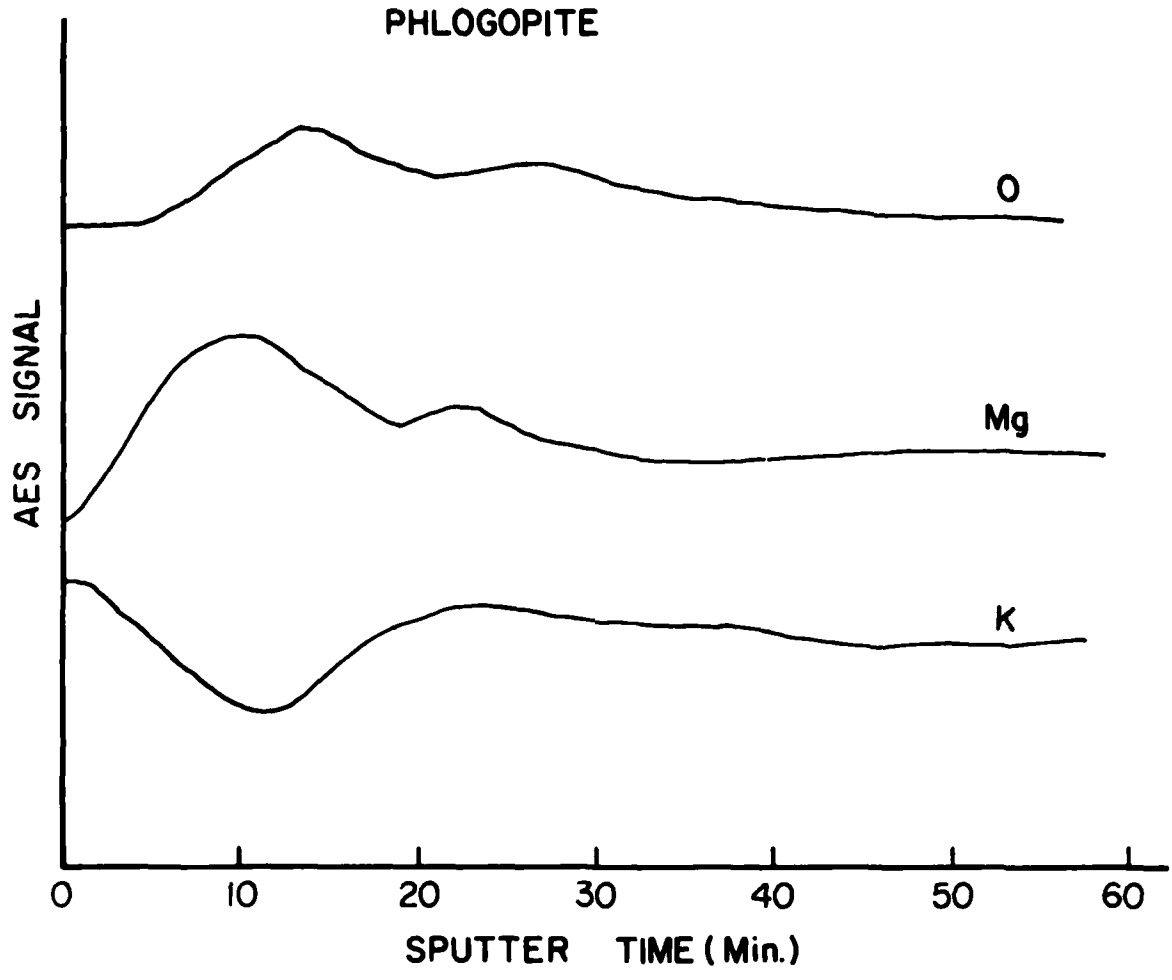

Figure 19. Distribution of Elements During He^+ Sputtering of Phlogopite from AES Data.

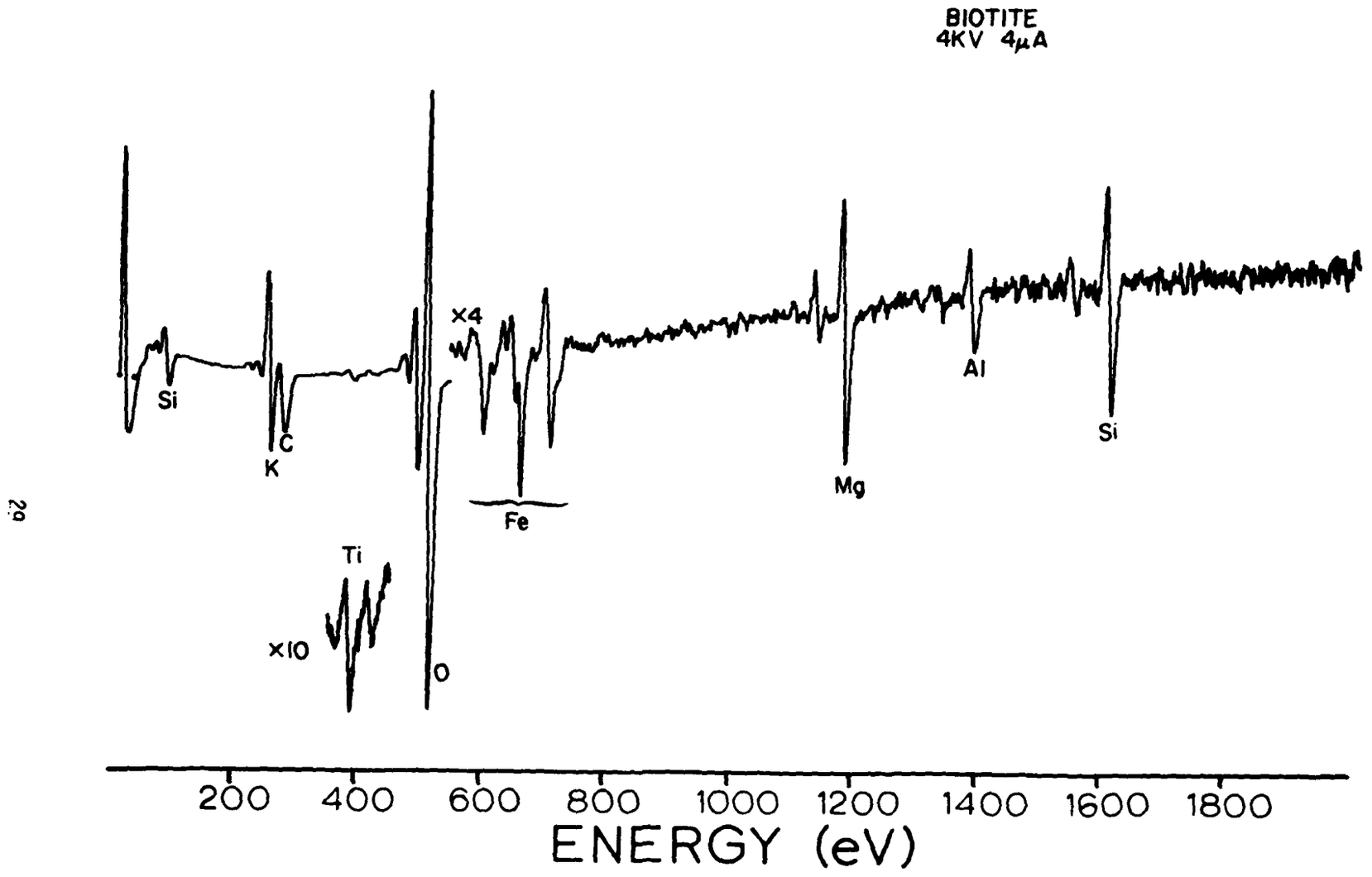

Figure 20. AES Data for Biotite.

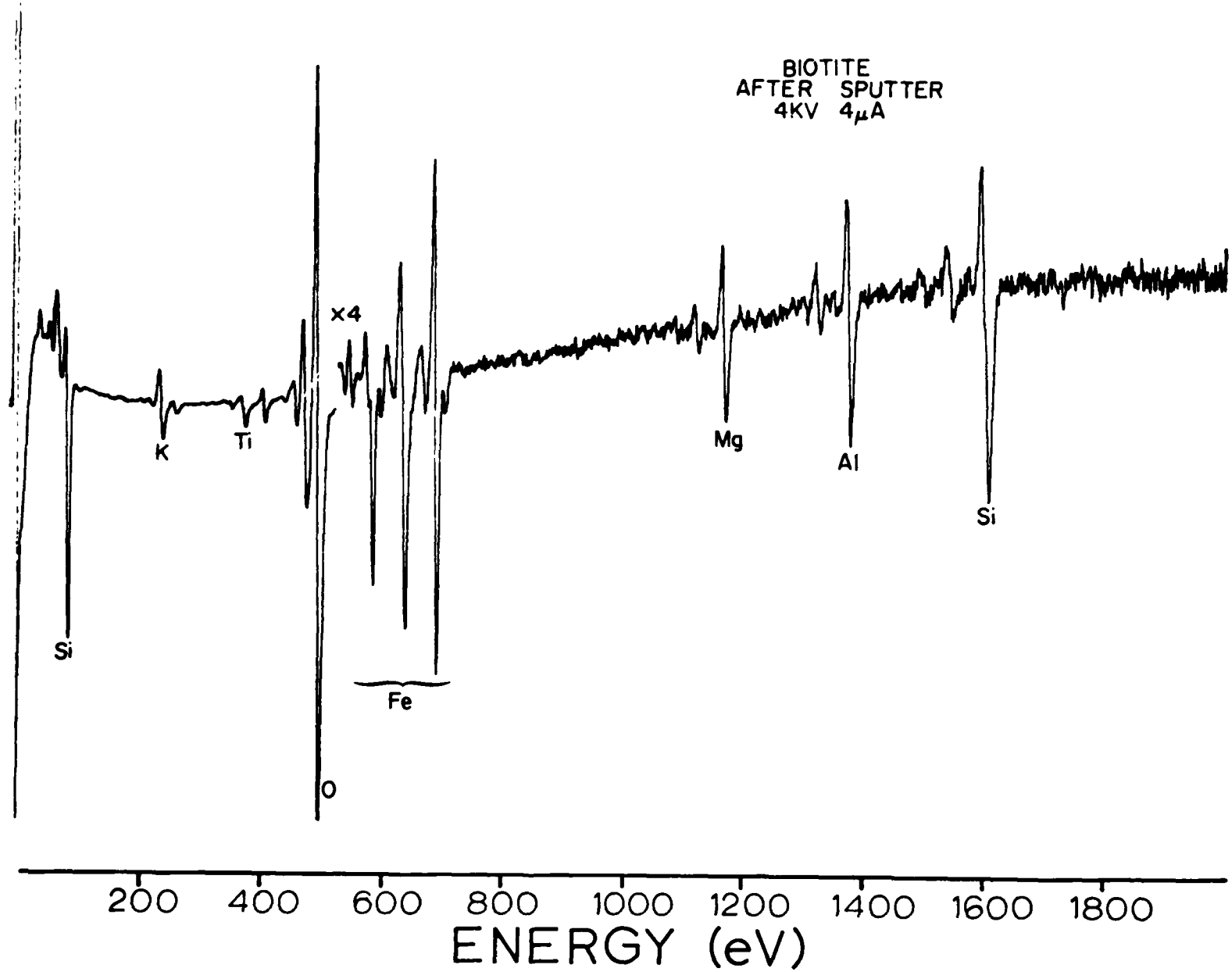

Figure 21. AES Data for Biotite after "Equilibrium Sputter".